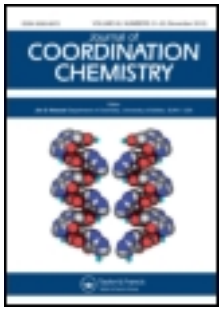

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Syntheses, crystal structures, and antibacterial activities of manganese(III), nickel(II), and copper(II) complexes containing a tetradentate Schiff base

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Three new mononuclear Schiff-base complexes, namely [Mn(L)Cl] (**1**), [Ni(L)] (**2**), and [Cu(L)] (**3**), where L = anion of [*N*,*N*′-bis(2-hydroxybenzophenylidene)]propane-1,2-diamine, have been synthesized by reacting equimolar amounts of the respective metal chloride and the tetradentate Schiff base, H_2L, in methanol. The complexes have been characterized by microanalytical, spectroscopic, single-crystal X-ray diffraction, and other physicochemical studies. Structural studies reveal that **1** adopts a distorted square-pyramidal geometry whereas **2** and **3** are isotypic with distorted square-planar geometries. The antibacterial activities of **1**–**3** along with their Schiff base have been tested against some Gram(+) and Gram(−) bacteria.

Keywords: Manganese(III); Nickel(II); Copper(II); Tetradentate Schiff base; Crystal structure; Antibacterial activity

1. Introduction

Schiff bases are useful chelating ligands in synthesis of transition metal complexes due to ease of preparation and structural varieties. Studies on such complexes of manganese, nickel, or copper have received overwhelming attention due to their important catalytic, magnetic, and biological properties [1–11]. Many Schiff bases obtained by condensation of diamines and salicylaldehyde or analogous carbonyl compounds have been used to synthesize manganese(III), nickel(II), and copper(II) complexes. However, transition metal complexes of the tetradentate Schiff base, derived from propane-1,2-diamine and 2-hydroxybenzophenone, have not received much attention. A limited number of transition metal complexes containing similar

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multidentate organic frameworks have been reported [12–17]. Due to their importance in bioinorganic chemistry, investigation of biological properties of such Schiff bases and their Mn(III), Ni(II), or Cu(II) complexes continues [18–29].

We describe the syntheses of three new mononuclear complexes of the same Schiff base with three first row transition metals. [Mn(L)Cl] (**1**), [Ni(L)] (**2**), and **[**Cu(L)] (**3**) were obtained by reaction of the corresponding metal chloride and the Schiff base (H_2L) in methanol. The complexes have been characterized by microanalytical, spectroscopic, and single-crystal X-ray diffraction studies. Structural studies indicate that **1** is comprised of discrete five-coordinate Mn(III) units with a distorted square-pyramidal geometry. In contrast, **2** and **3** are isotypic and adopt distorted square-planar geometries around each metal ion, namely Ni(II) in **2** and Cu(II) in **3**. In addition to the physicochemical studies, **1**–**3** have been tested *in vitro* to assess their antibacterial activities against some common reference bacteria and the results were compared with similar doses of two commercial antibiotics, namely Gatifloxacin and Ciprofloxacin.

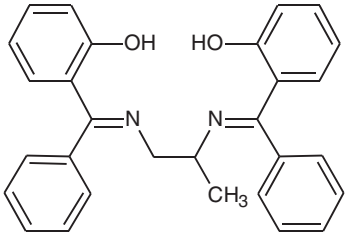
2. Experimental

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Perkin-Elmer 2400-II elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 65 FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). Room-temperature solid-phase magnetic susceptibilities were measured at 298 K with a PAR 155 vibrating sample magnetometer with $Hg[Co(NCS)_4]$ as the calibrant. Diamagnetic corrections were calculated from Pascal's constants. Molar conductances of the complexes in dry methanol were measured using a direct reading conductivity meter of Systronics (Type 304).

2.2. *Materials*

Commercially available reagent grade 2-hydroxybenzophenone, 1,2-diaminopropane, manganese(II) chloride tetrahydrate, nickel(II) chloride hexahydrate, copper(II) chloride dihydrate, and methanol were used without purification. The tetradentate Schiff base, H_2L, was obtained by condensation of 1,2-diaminopropane with 2-hydroxybenzophenone using similar methods as described earlier [30].



H_2L

2.3. *Syntheses of 1–3*

Complexes **1**–**3** were prepared by mixing the respective metal chloride with the Schiff base in 1 : 1 molar ratio in methanol followed by slow evaporation. For **1**, a methanolic solution (10 mL) of H_2L (0.22 g, 0.5 mmol) was added dropwise to a methanolic solution (10 mL) of $MnCl_2 \cdot 4H_2O$ (0.1 g, 0.5 mmol) with constant stirring at room temperature. Stirring was continued for 15 min and the resulting deep brown solution was left for slow evaporation at room temperature in a beaker open to the atmosphere. After a week, deep brown crystals of **1** appeared. The crystals were collected by filtration, washed with methanol, and finally dried. Yield: 0.16 g (61%). The synthetic route described for **1** was followed in the preparation of **2** and **3**, except that 10 mL methanolic solution of $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol) for **2** or $CuCl_2 \cdot 2H_2O$ (0.09 g, 0.5 mmol) for **3** was used instead of the manganese salt. Bright red crystals of **2** and blue crystals of **3** were obtained after 8–10 days. Yields of **2** and **3** were 0.14 g (57%) and 0.12 g (48%), respectively. Anal. Calcd for $C_{29}H_{24}ClMnN_2O_2$ (**1**) (%): C, 66.61; H, 4.63; N, 5.36. Found (%): C, 66.56; H, 4.58; N, 5.32. FTIR (KBr, cm^{-1}): 1598(s), 1579(s), 1530(s), 1489(m), 1460(m), 1440(s), 1430(m), 1330(s), 1239(m), 1146(s), 847(m), 755(s), 707(m), 622(m). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 5. μ_{eff} (RT, BM): 4.83. Anal. Calcd for $C_{29}H_{24}N_2NiO_2$ (**2**) (%): C, 70.91; H, 4.92; N, 5.70. Found (%): C, 71.06; H, 4.93; N, 5.72. FTIR (KBr, cm^{-1}): 1599(s), 1580(s), 1530(s), 1458(m), 1439(s), 1431(m), 1347(s), 1242(s), 1134(m), 1008(w), 842(m), 759(s), 707(m), 604(w). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 7. Diamagnetic. Anal. Calcd for $C_{29}H_{24}CuN_2O_2$ (**3**) (%): C, 70.22; H, 4.88; N, 5.65. Found (%): C, 69.94; H, 4.85; N, 5.72. FTIR (KBr, cm^{-1}): 1598(s), 1579(s), 1530(s), 1458(m), 1439(s), 1431(m), 1347(s), 1257(m), 1242(s), 1138(m), 841(m), 759(s), 707(m), 604(w). Λ_M (MeOH, $\Omega^{-1}\,cm^2\,mol^{-1}$): 6. μ_{eff} (RT, BM): 1.74.

2.4. *Crystal structure determination and refinement*

For X-ray diffraction studies, suitable single crystals of **1**–**3** with approximate dimensions of $0.15 \times 0.27 \times 0.36$, $0.60 \times 0.82 \times 0.95$, and $0.08 \times 0.10 \times 0.10\,mm^3$, respectively, were mounted on a Bruker-Nonius Kappa diffractometer equipped with a CCD area detector and employing graphite-monochromated Mo-Kα radiation. The reflection data were collected and processed using the Bruker-Nonius program suites COLLECT, DENZO-SMN, and related analysis software [31–35]. The structures were solved by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F^2 using SHELX [36]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were partially located from the difference Fourier maps, partially placed geometrically and refined keeping restraints (riding mode). For **2** and **3**, several carbon and hydrogen atoms showed disorder between two distinct positions. Initially, the occupation parameters for these disordered atoms were refined freely but when it turned out to be refined around 1/2, they were fixed at this value. A summary of the crystallographic data, structural parameters, and refinement details for the compounds is presented in table 1.

Table 1. Crystallographic data and refinement parameters for **1–3**.

Parameters	**1**	**2**	**3**
Formula	$C_{29}H_{24}ClMnN_2O_2$	$C_{29}H_{24}N_2NiO_2$	$C_{29}H_{24}CuN_2O_2$
Formula weight ($g\,mol^{-1}$)	522.90	491.21	496.04
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions (Å, °)			
a	11.185(1)	9.781(2)	9.792(2)
b	17.662(2)	15.448(3)	15.444(3)
c	12.617(1)	15.789(3)	15.806(3)
α	90	90	90
β	92.36(1)	90	90
γ	90	90	90
Volume ($Å^3$), Z	2490.2(3), 4	2385.7(8), 4	2390.3(8), 4
Calculated density ($g\,cm^{-3}$)	1.40	1.37	1.38
Absorption coefficient (mm^{-1})	0.67	0.84	0.94
$F(000)$	1080	1024	1028
hkl range	$-11 \le h \le 14$; $-24 \le k \le 23$; $-16 \le l \le 17$	$-14 \le h \le 14$; $-22 \le k \le 22$; $-23 \le l \le 23$	$-14 \le h \le 14$; $-23 \le k \le 23$; $-23 \le l \le 23$
Temperature (K)	110(2)	296(2)	296(2)
Wavelength (Mo-Kα) (Å)	0.71069	0.71073	0.71073
Reflections measured	16,767	8244	27,914
Reflections unique	6048	8244	8268
Data with $F_o > 4\sigma(F_o)$	4997	4605	6155
R_{int}	0.094	0.124	0.065
Parameters refined	316	356	356
R^a $F_o > 4\sigma(F_o)$	0.078	0.057	0.041
wR^b	0.091	0.117	0.098
Flack parameters	–	0.06(2)	0.02(1)
S	1.078	1.150	1.021
$\Delta\rho_{max}/\Delta\rho_{min}$ ($e\,Å^{-3}$)	1.68 and −0.87	0.47 and −0.41	0.34 and −0.40

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P]$, $P = (F_o^2 + 2F_c^2)/3$.

2.5. *Antibacterial screening*

Antibiograms of **1–3** and two reference commercial antibiotics, namely Gatifloxacin and Ciprofloxacin (purchased in powder form from Span Diagnostic Limited, Surat, India), were prepared against two Gram-positive bacteria (*Staphylococcus aureus* MTCC 2940 and *Bacillus subtilis* MTCC 441) and two Gram-negative bacteria (*Pseudomonas aeruginosa* MTCC 2453 and *Escherichia coli* MTCC 739) using the agar well diffusion method on nutrient agar medium with necessary modifications [37]. During the experiment, the test microbes were removed from the slant aseptically with inoculating loops and transferred to separate test tubes containing 5.0 mL of saline solution (0.85% NaCl). Sufficient inoculums were then added to adjust the turbidity to 0.5 McFarland (10^8 CFU mL^{-1}), as recorded in a digital colony counter. For each bacterium, 1.0 mL of the suspension was added to 15–20 mL of nutrient agar and transferred to an agar plate of 9.0 cm diameter. The antibacterial activities of the compounds were tested after cooling the inoculated agar at room temperature for 25 min. The antibacterial activities of propane-1,2-diamine (DAP), 2-hydroxybenzophenone (HBP) and H_2L were also evaluated during the same experiment. All the compounds including the antibiotics were dissolved in DMSO to prepare five different

concentrations (0.2, 0.4, 0.6, 0.8, and 1.0 mg mL^{-1}) for evaluation of limiting doses. Wells of 0.6 cm diameter were pierced in the agar and filled with the test compounds of varied concentrations and incubated for 24 h at 303 K for *B. subtilis* and at 310 K for all other bacteria. Antibacterial activities were evaluated by measuring the inhibition zone diameters (IZDs) and their minimum inhibitory concentrations (MICs). MIC is the lowest concentration of a compound in DMSO that exhibited no visual growth of the organisms in the culture tubes. Such value of the test compounds was determined by the serial dilution technique adopted by the National Committee for Clinical Laboratory Standards [38]. Each of the above experiments was repeated thrice along with a control set using DMSO. The mean value obtained for three individual replicates was then used to calculate the growth inhibition zone of each sample.

3. Results and discussion

3.1. *Syntheses*

Complexes **1**–**3** were obtained by reaction of the respective metal chloride with a tetradentate Schiff base in 1 : 1 molar ratio in methanol. Mn^{II} underwent aerial oxidation to Mn^{III} during formation of **1** to form a more stable complex with ligand containing harder donors [30, 39]. As a result, the pentacoordinate **1** has Mn(III) with a square-pyramidal geometry with a chloride in the apical position. However, both Ni(II) and Cu(II) formed square planar **2** and **3**, respectively, containing the NNOO donor Schiff base only. The complexes have been characterized by elemental analysis, IR spectroscopy, electrical conductivity, and magnetic susceptibility as well as by single-crystal X-ray structural analysis. In methanol, these compounds behave as non-electrolytes as evident from Λ_M values (*ca* 5–7 Ω^{-1} cm^2 mol^{-1}). Room-temperature magnetic susceptibility measurements show that **1** and **3** possess magnetic moment values of 4.83 and 1.74 B.M., respectively, close to the spin-only values of Mn(III) and Cu(II). These observations are consistent with discrete and magnetically non-coupled d^4 system in **1** and d^9 system in **3**. As expected, **2** is diamagnetic showing square-planar low spin $3d^8$ system. All these results along with those of X-ray structural analysis are consistent with the proposed mononuclear formulae of **1**–**3**.

3.2. *FTIR spectra*

Infrared spectra of **1**–**3** have some common features as expected from their structural similarities. All exhibit strong absorptions at 1579–1580 and 1598–1599 cm^{-1} corresponding to C=N stretch [ν_{CN}] of the Schiff-base ligands. All other vibrations including the phenolic C–O stretch of metal-bound Schiff bases are located in the range 600–1600 cm^{-1}, in agreement [40] with the respective structural features of the Schiff-base complexes.

3.3. *Crystal structures of 1–3*

The molecular structures of **1**–**3** are displayed in figure 1 and some selected bond distances and angles are listed in table 2. The molecular unit of each complex can be

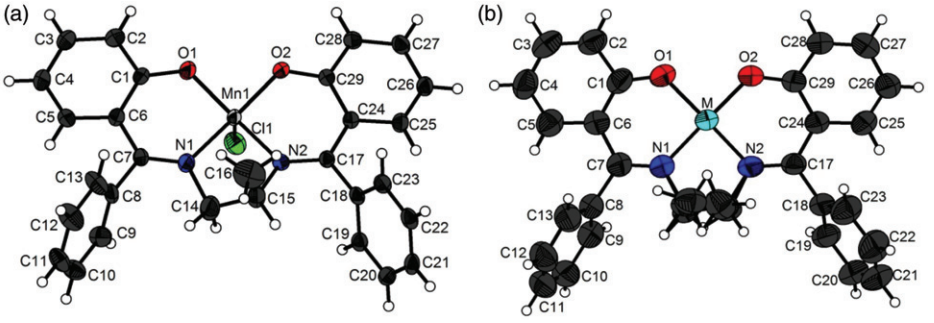


Figure 1. Molecular structures of (a) **1** and (b) **2** ($M = Ni^{2+}$) or **3** ($M = Cu^{2+}$).

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

1		**2**		**3**	
Mn1–O1	1.864(2)	Ni1–O1	1.887(2)	Cu1–O1	1.886(2)
Mn1–N1	2.002(3)	Ni1–N1	1.934(3)	Cu1–N1	1.942(2)
Mn1–N2	2.001(3)	Ni1–N2	1.944(3)	Cu1–N2	1.943(2)
Mn1–O2	1.873(2)	Ni1–O2	1.877(2)	Cu1–O2	1.877(2)
Mn1–Cl1	2.355(1)				
O1–Mn1–O2	89.56(1)	O1–Ni1–O2	88.98(1)	O1–Cu1–O2	88.84(8)
O1–Mn1–N1	90.08(1)	O1–Ni1–N1	92.25(1)	O1–Cu1–N1	92.66(9)
O1–Mn1–N2	158.66(1)	O1–Ni1–N2	178.61(1)	O1–Cu1–N2	178.25(9)
O2–Mn1–N1	158.67(1)	O2–Ni1–N1	178.73(1)	O2–Cu1–N1	178.43(9)
O2–Mn1–N2	89.26(1)	O2–Ni1–N2	92.34(1)	O2–Cu1–N2	92.89(8)
N1–Mn1–N2	83.42(1)	N1–Ni1–N2	86.42(1)	N1–Cu1–N2	85.61(9)
Cl1–Mn1–O2	101.57(8)				
Cl1–Mn1–N2	101.06(9)				
Cl1–Mn1–N1	99.49(1)				
Cl1–Mn1–O1	100.05(1)				

described as a butterfly-like arrangement around a metal cation by the Schiff-base anion (L^{2-}) with four of its aromatic rings disposed as wings. X-ray studies reveal that each central ion in **1–3** is a member of one five-membered and two six-membered rings. A distorted square-pyramidal geometry is adopted by **1**, whereas **2** and **3** are distorted square planar. The torsion angles (O1–N1–N2–O2) for **1**, **2**, and **3** are −0.07, 0.13, and −0.16°, respectively. The irregular five-coordinate environment (figure 1a) around Mn(III) in **1** is maintained by a chloride (Cl1) at the apical position and two imino nitrogen atoms (N1, N2) plus two phenolate oxygen atoms (O1, O2) in the basal plane. As expected, the Mn–N bond distances are greater than Mn–O bonds; bond distances ranging from 1.864 to 2.002 Å agree well with similar Schiff-base complexes of manganese(III) [20, 39]. Distortion in the coordination sphere of Mn(III) from ideal geometry is obvious due to structural constraints imposed by the polydentate ligand framework. However, distortion is less pronounced in **1** as reflected by *cisoid* and *transoid* angles, being much closer to the ideal values. The observed bond angles thus indicate that Mn(III) is slightly above the square base.

Apart from the additional chloride which gives a different geometry of **1**, there is another notable difference between **1** and **2** or **3** (figure 1). The isopropyl part between

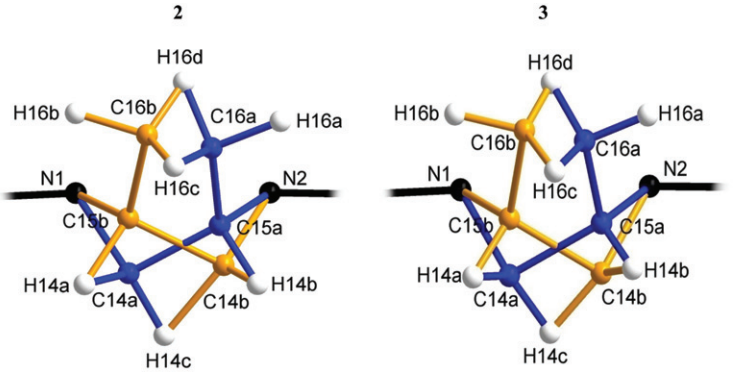


Figure 2. Disordered parts of **2** and **3** in ball-and-stick representation. Isopropyl chains containing the carbon atoms C14, C15, and C16 (labeled a or b) are half-occupied. Notice that some hydrogen atoms (H16a, H16b) belong only to one half, i.e. half-occupied, while others belong to both positions (H14a, H14b, H14c, H16c, H16d), i.e. fully occupied.

the imino nitrogen atoms of the Schiff base is disordered in both **2** and **3** (figure 2). While the position of C16 of the methyl group is clearly located in **1**, there are two different half-occupied positions for this atom in **2** and **3** (labeled as C16a and b in figure 2). Thus, the C16 atom as well as the whole isopropyl chain is split between two positions. In each molecule of the lattice, the chain faces either from left to right or from right to left. These two alternatively occupied chains or orientations are represented by the atoms C14a, C15a, C16a in one case and C14b, C15b, C16b in the other (figure 2). As a consequence of this disorder, hydrogen atoms of this part of the molecule are also disordered. Five hydrogen positions overlap in both configurations and hence H14a, H14b, H14c, H16c, and H16d are fully occupied. Although these atoms may not share the same positions exactly, it was impossible to distinguish two slightly overlapping, half-occupied hydrogen positions in the refinement. Hydrogen atoms H16a and H16b are properly half-occupied since these are realized only in one conformation. As the same disorder was found in both **2** and **3**, they were modeled independently to obtain virtually the same geometry of the Ni(II) and Cu(II) complexes.

Unaffected by the above disorder, M (where $M = Ni^{2+}$ in **2** and Cu^{2+} in **3)** is coordinated by the tetradentate Schiff base in the same manner as for **1** to form the square base (figure 1). Thus, in both **2** and **3**, MN_2O_2 chromophores constitute the distorted square-planar arrangement in which the four coordination of the metal is completed by the same two imino nitrogen atoms (N1, N2) and two phenolate oxygen atoms (O1, O2) donated by L^{2-}. Although both **2** and **3** undergo slight distortions from ideal geometry due to the asymmetric nature of the Schiff base, they are isotypic, which is reflected in their very similar magnitudes of bond parameters. All relevant bond distances and angles are also comparable to other analogous Schiff-base complexes of Ni(II) and Cu(II) [6–10].

The crystal packing diagrams of **1**–**3** are presented in figure 3. The molecules are packed rather loosely in herringbone patterns and isolated from each other in their crystal lattices. Weak intermolecular van der Waals and $\pi\cdots\pi$ interactions are operative to hold the molecules together in the solid state.

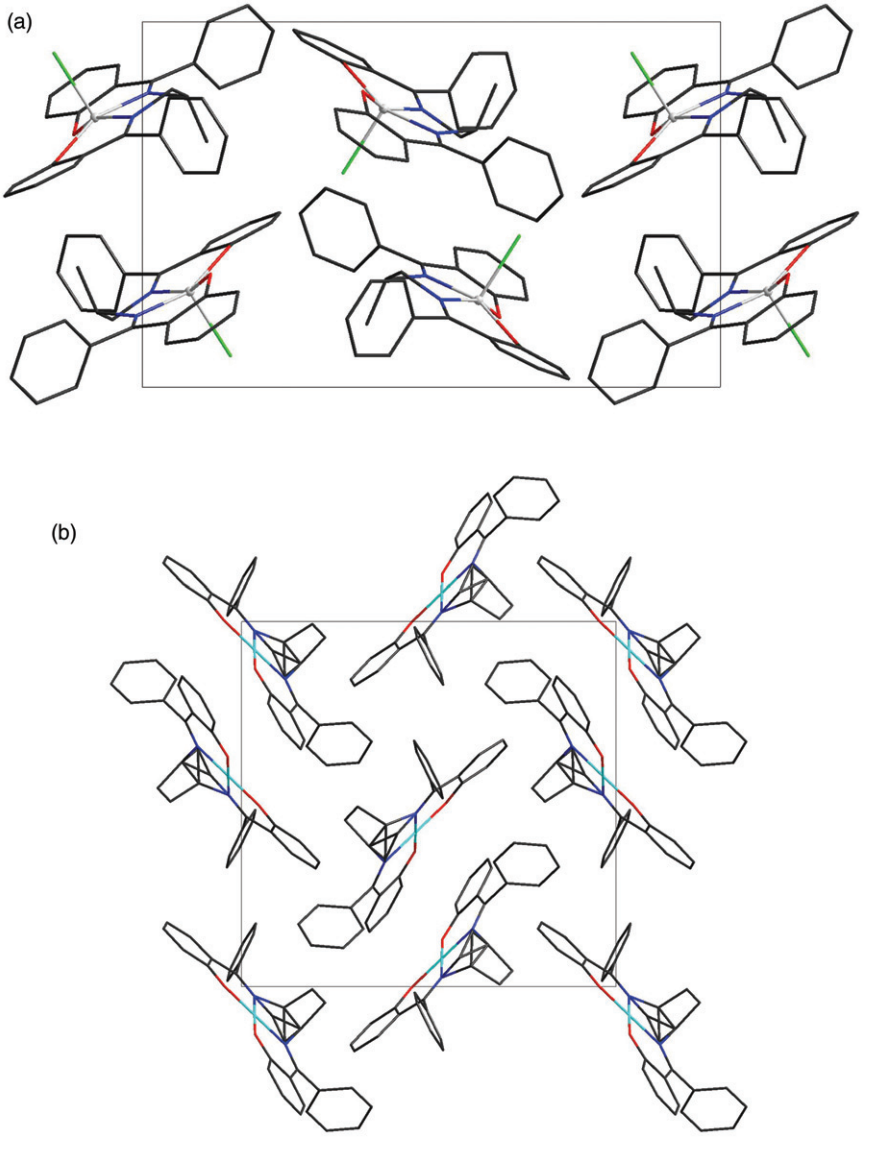


Figure 3. Structural packing diagrams of (a) **1** viewed along [0 0 1] direction and (b) **2** or **3** viewed along [1 0 0] direction. Hydrogen atoms are omitted for clarity.

3.4. *Antibacterial activities of the compounds*

The antibacterial potential of the compounds against four chosen bacteria is presented as their IZD and MIC values in tables 3 and 4, respectively. The results of the antibacterial screening indicate that **1**–**3** exhibit broad spectrum antibacterial activity against all four reference bacteria. However, they possess rather high MIC and low IZD values. The highest IZD and lowest MIC values are observed in **2** and **3**, suggesting that the Ni(II) and Cu(II) complexes are most susceptible to the reference bacteria. Although both **2** and **3** are more active toward *S. aureus*, **2** possesses better bactericidal

Table 3. Antibacterial activities of **1–3** and related compounds compared to control and standard antibiotics.

		IZD (mean ± standard error) (cm)			
		Gram-positive bacteria		Gram-negative bacteria	
Compounds	Dose (mg mL^{-1})	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*E. coli*
1	1.0	1.4 ± 0.3	1.2 ± 0.3	1.4 ± 0.6	1.4 ± 0.3
	0.8	1.1 ± 0.3	–	1.1 ± 0.3	1.1 ± 0.3
	0.6, 0.4, 0.2	–	–	–	–
2	1.0	1.9 ± 0.7	1.9 ± 0.7	1.8 ± 0.3	1.6 ± 0.3
	0.8	1.5 ± 0.3	1.6 ± 0.3	1.4 ± 0.7	1.4 ± 0.3
	0.6	1.4 ± 0.3	1.3 ± 0.6	1.2 ± 0.3	1.1 ± 0.3
	0.4	1.0 ± 0.3	1.1 ± 0.3	1.000 ± 0.000	–
	0.2	–	–	–	–
3	1.0	2.0 ± 0.3	1.6 ± 0.3	1.7 ± 0.6	1.6 ± 0.3
	0.8	1.6 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.3 ± 0.6
	0.6	1.4 ± 0.3	1.1 ± 0.3	1.1 ± 0.3	1.2 ± 0.3
	0.4	1.4 ± 0.3	1.1 ± 0.3	1.1 ± 0.3	1.000 ± 0.000
	0.2	1.1 ± 0.3	–	1.000 ± 0.000	–
H_2L	1.0	1.3 ± 0.6	1.4 ± 0.3	1.3 ± 0.3	1.4 ± 0.3
	0.8	1.2 ± 0.3	1.1 ± 0.3	1.2 ± 0.3	1.1 ± 0.3
	0.6	1.2 ± 0.3	–	–	1.1 ± 0.3
	0.4	1.000 ± 0.000	–	–	1.000 ± 0.000
	0.2	–	–	–	–
DAP	1.0	1.2 ± 0.3	–	–	1.2 ± 0.3
	0.8	1.1 ± 0.3	–	–	1.000 ± 0.000
	0.6, 0.4, 0.2	–	–	–	–
HBP	1.0	–	1.1 ± 0.3	1.1 ± 0.3	–
	0.8	–	1.1 ± 0.3	1.000 ± 0.000	–
	0.6, 0.4, 0.2	–	–	–	–
Gatifloxacin	1.0	2.6 ± 0.6	2.7 ± 0.6	2.5 ± 0.3	2.6 ± 0.3
	0.8	2.2 ± 0.3	2.2 ± 0.3	2.2 ± 0.3	2.4 ± 0.7
	0.6	2.0 ± 0.7	1.9 ± 0.7	1.8 ± 0.3	2.0 ± 0.3
	0.4	1.9 ± 0.7	1.6 ± 0.3	1.5 ± 0.3	1.6 ± 0.3
	0.2	1.6 ± 0.3	1.4 ± 0.3	1.4 ± 0.3	1.4 ± 0.3
Ciprofloxacin	1.0	2.4 ± 0.6	2.3 ± 0.3	2.1 ± 0.3	2.6 ± 0.3
	0.8	2.1 ± 0.7	2.2 ± 0.3	2.0 ± 0.3	2.4 ± 0.6
	0.6	1.8 ± 0.7	1.8 ± 0.3	1.7 ± 0.3	1.9 ± 0.7
	0.4	1.5 ± 0.3	1.4 ± 0.7	1.4 ± 0.3	1.4 ± 0.3
	0.2	1.1 ± 0.3	1.2 ± 0.3	1.1 ± 0.3	1.000 ± 0.000
Control (DMSO)	0.2–1.0	–	–	–	–

property than **3** against *B. subtilis* and *P. aeruginosa*. In contrast, **1** exhibits very poor antibacterial activity against all the bacteria and its MIC values are quite high. The antibacterial properties of **2** and **3** are appreciably higher but that of **1** does not differ much from the Schiff base (H_2L). Although the Schiff base is mildly active against the bacteria at rather high concentrations, its constituents are not very active. The IZD data show that DAP is active against *S. aureus* and *E. coli* but is inactive against *B. subtilis* or *P. aeruginosa* whereas the reverse is seen for HBP. Among all the bacteria, *E. coli* is least susceptible against all the complexes.

Table 4. MIC values (mg mL^{-1}) of **1–3** for different bacteria.

Compounds	*S. aureus*	*B. subtilis*	*P. aeruginosa*	*E. coli*
1	<0.8	<1.0	<0.8	<0.8
2	<0.4	<0.4	<0.4	<0.6
3	<0.2	<0.4	<0.2	<0.4
H_2L	<0.4	<0.8	<0.8	<0.4
DAP	<0.8	>1.0	>1.0	<0.8
HBP	>1.0	<0.8	<0.8	>1.0
Gatifloxacin	<0.2	<0.2	<0.2	<0.2
Ciprofloxacin	<0.2	<0.2	<0.2	<0.2

From the *in vitro* antibacterial assay, most of the tested compounds are found to possess mild to moderate antibacterial activities which increase with dose. However, the activities are much lower than those of the tested commercial antibiotics at similar concentrations. These results suggest that antibacterial activities of the complexes are affected by ligand as well as metal ions. These observations are similar to earlier reports [18–29] of bioactivities of analogous first row transition metal Schiff-base complexes.

4. Conclusion

Synthesis and characterization of mononuclear Schiff-base complexes of three first row transition metals containing a less-studied tetradentate Schiff base are described in this article. The same reaction mixture yielded a square-pyramidal complex in the presence of $MnCl_2$ and square-planar complexes in the presence of either $NiCl_2$ or $CuCl_2$. Antibacterial screening of the compounds indicate mild to moderate bactericidal activities which are comparable to those of the previously reported Mn(III), Ni(II), and Cu(II) Schiff-base complexes [18–29]. In addition to the synthetic and structural investigations, this study describes the antibacterial potential of a Schiff base and its complexes.

Supplementary material

CCDC 855 538–855540 contain the supplementary crystallographic data for **1–3**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk

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